SUPPORTING INFORMATION

Boron clusters (ferrabisdicarbollides), shaping the future as radiosensitizers for multimodal (chemo/radio/PBFR) therapy of glioblastoma.

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Scheme S.1.- Synthesis of Cs[8,8'-I_2-*o*-FESAN] and Na[8,8'-I_2-*o*-FESAN. a) N-iodosuccinidide in Et(OH); b) cationic exchange resin.[i] Circles in grey represent the C_c-H vertices, the orange ones correspond to Fe^{3+} while the circles in dark and light pink correspond to B-H and B-I vertices, respectively.

Figure S1. UV-visible spectra of the ferrabis(dicarbollides) in 0.08 mM aqueous solution: in red, Na[*o*-FESAN] and in dashed red its peaks' deconvolution at 271 and 295 nm; in green, Na[8,8'-I_2-*o*-FESAN] and in dashed green its peaks' deconvolution at 289 and 343 nm.

Figure S2. Spectra of Na[*o*-FESAN] and Na[8,8'-I_2-*o*-FESAN] in powder and cavity background signal. Values of the *g* factors indicated by numbers are following: 1=4.7, 2=3.7, 3=2.7 and 4=2.0.

Figure S3.- TGA/DSC of Na[*o*-FESAN].

Figure S4.- TGA/DSC of Na[8,8'-I_2-*o*-FESAN].

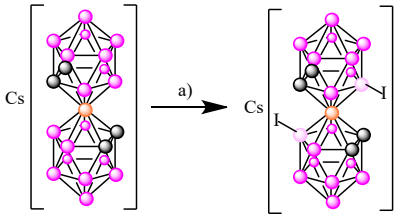
Figure S5.- a) $^{11}B\{^1H\}$-NMR spectra of 2 mM of Na[*o*-FESAN] in aqueous solution (blue), in 0.1M phosphate buffer (green), in DMEM (red), DMEM + 10% FBS (purple); the spectra were run with a relaxation time parameter of 2.62 s.

Figure S6.- a) $^{11}B\{^1H\}$-NMR spectra of 2 mM of Na[*o*-FESAN] in aqueous solution (blue), in 0.1M phosphate buffer (green), in DMEM (red), DMEM + 10% FBS (purple); the spectra were run with a relaxation time parameter of 0.015 s.

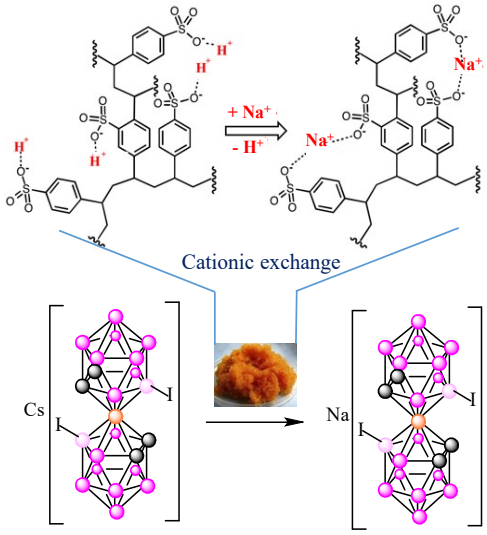
Figure S7.- DLS measurements of aqueous solution of 2 mM of Na[*o*-FESAN] in blue, in 0.1M phosphate buffer (green), in DMEM (red), in DMEM + 10% FBS (purple). DMEM + 10% FBS (black).

Scheme S1.- Synthesis of Cs[8,8'-I_2-*o*-FESAN] and Na[8,8'-I_2-*o*-FESAN. a) N-iodosuccinidide in Et(OH); b) cationic exchange resin.[i] Circles in grey represent the C_c-H vertices, the orange ones correspond to Fe^{3+} while the circles in dark and light pink correspond to B-H and B-I vertices, respectively.

a)



b)



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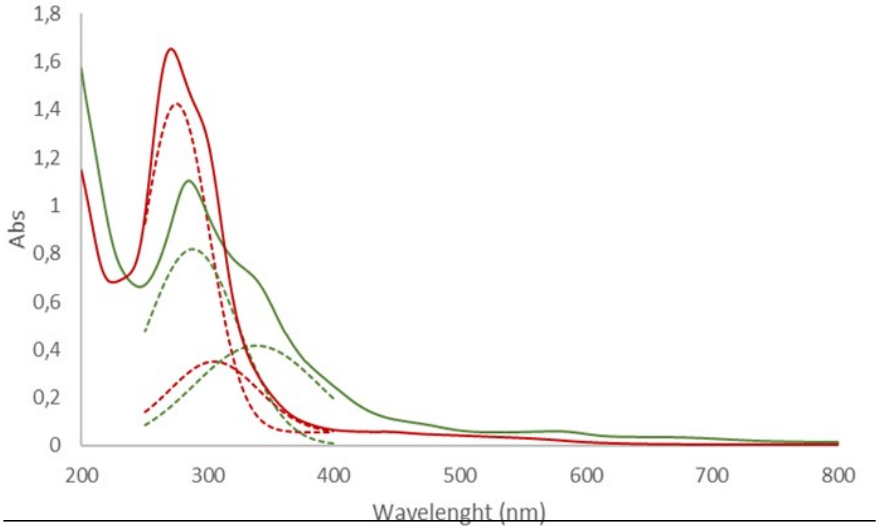


Figure S2. Spectra of Na[*o*-FESAN] and Na[8,8'-I_2-*o*-FESAN] in powder and cavity background signal. Values of the *g* factors indicated by numbers are following: 1=4.7, 2=3.7, 3=2.7 and 4=2.0.

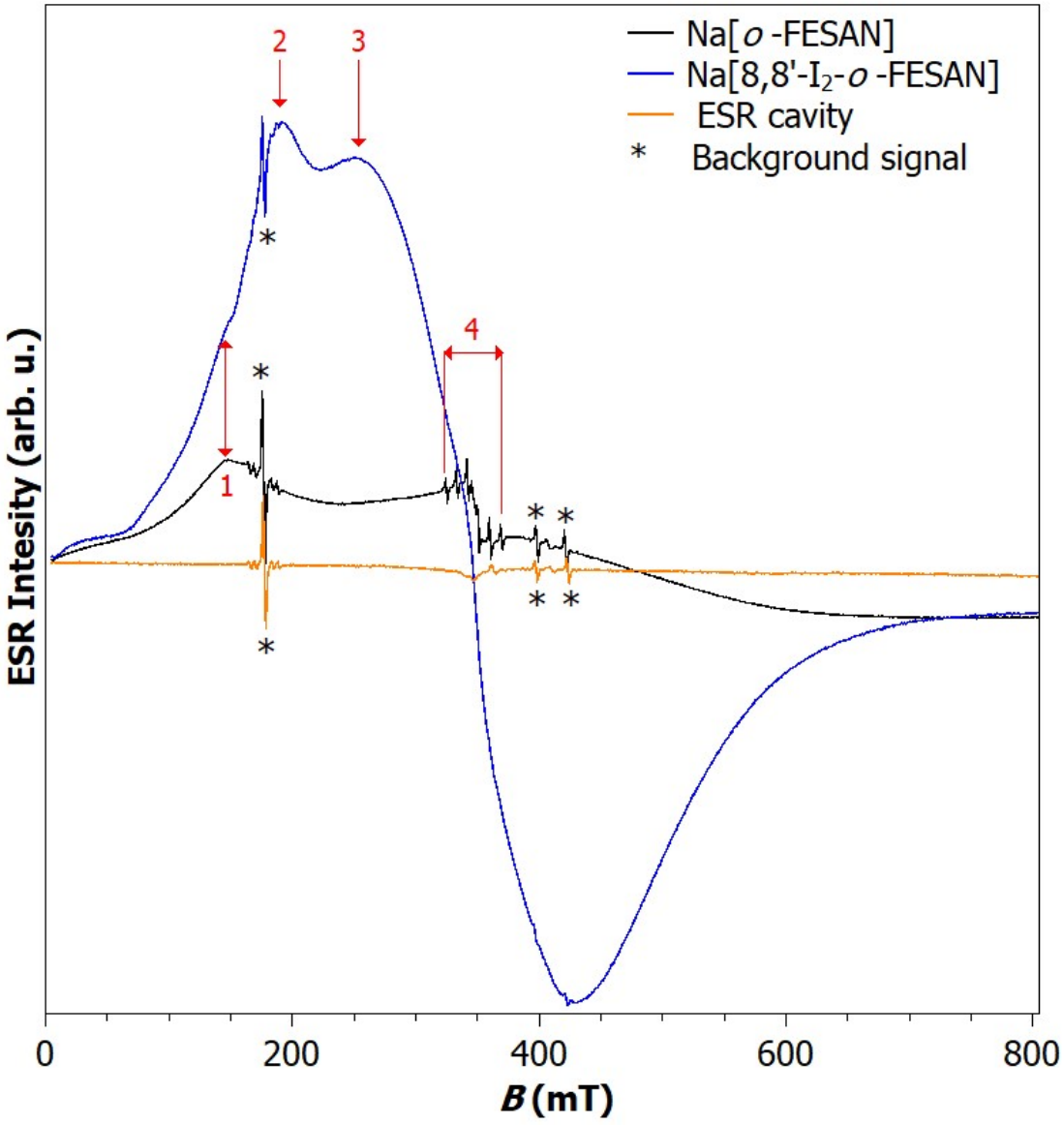


Figure S3.- TGA/DSC of Na[*o*-FESAN].

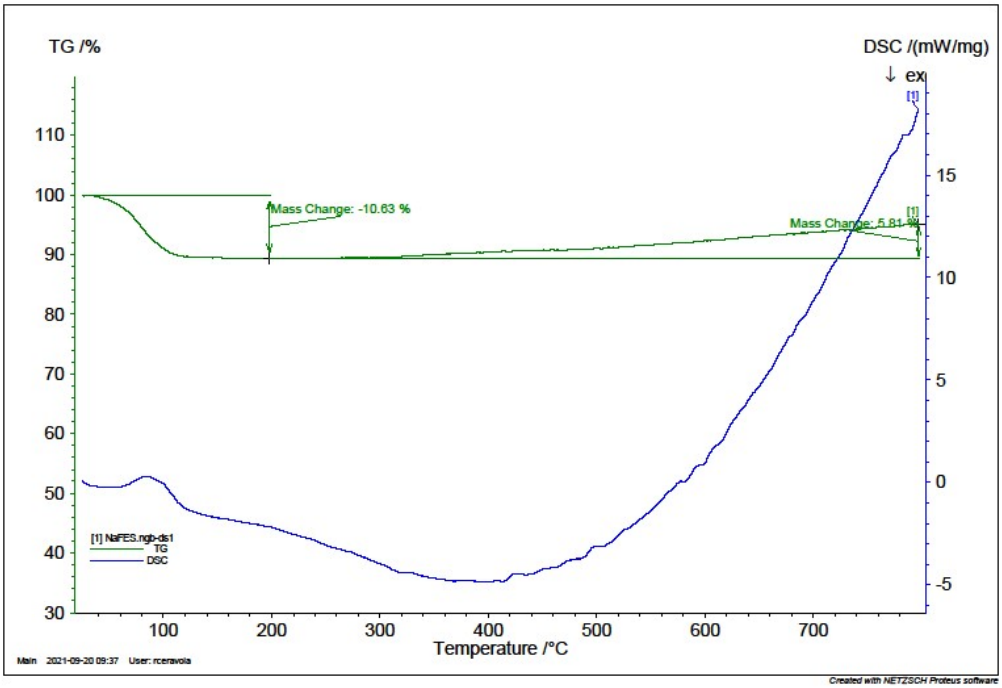


Figure S4.- TGA/DSC of Na[8,8'-I_2-*o*-FESAN].

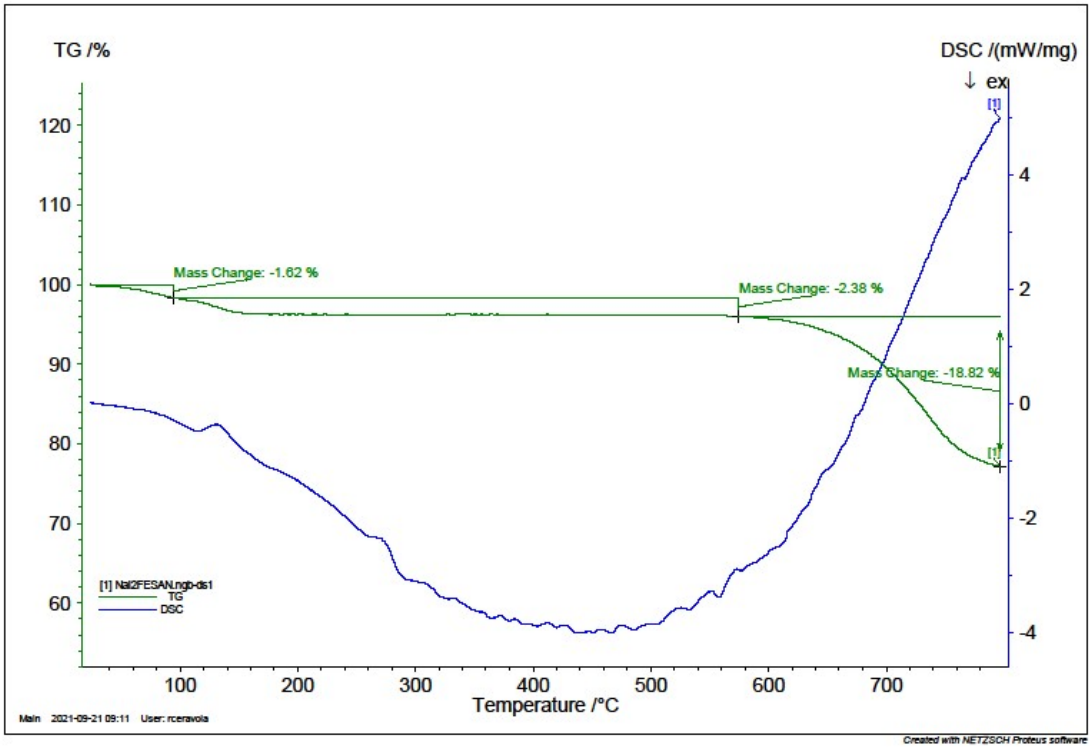


Figure S5.- a) $^{11}B\{^{1}H\}$-NMR spectra of 2 mM of Na[*o*-FESAN] in aqueous solution (blue), in 0.1M phosphate buffer (green), in DMEM (red), DMEM + 10% FBS (purple); the spectra were run with a relaxation time parameter of 2.62 s.

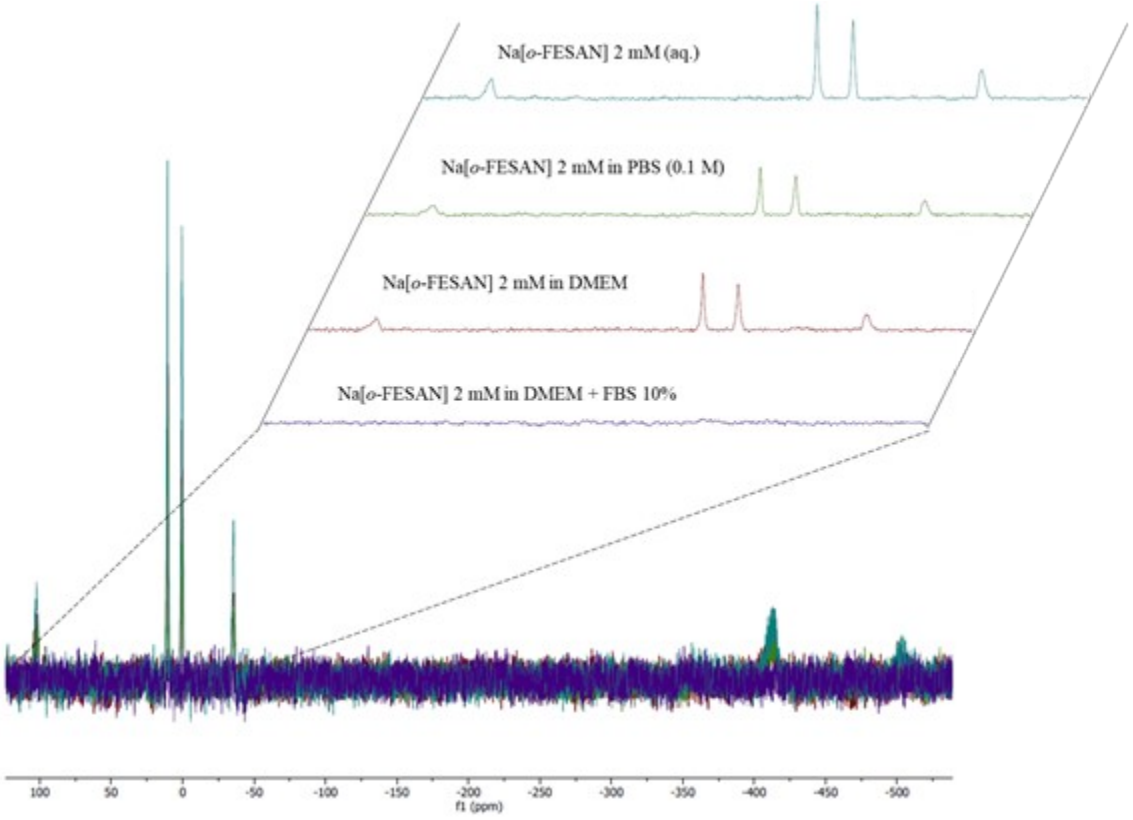


Figure S6.- a) $^{11}B\{^{1}H\}$-NMR spectra of 2 mM of Na[*o*-FESAN] in aqueous solution (blue), in 0.1M phosphate buffer (green), in DMEM (red), DMEM + 10% FBS (purple); the spectra were run with a relaxation time parameter of 0.015 s.

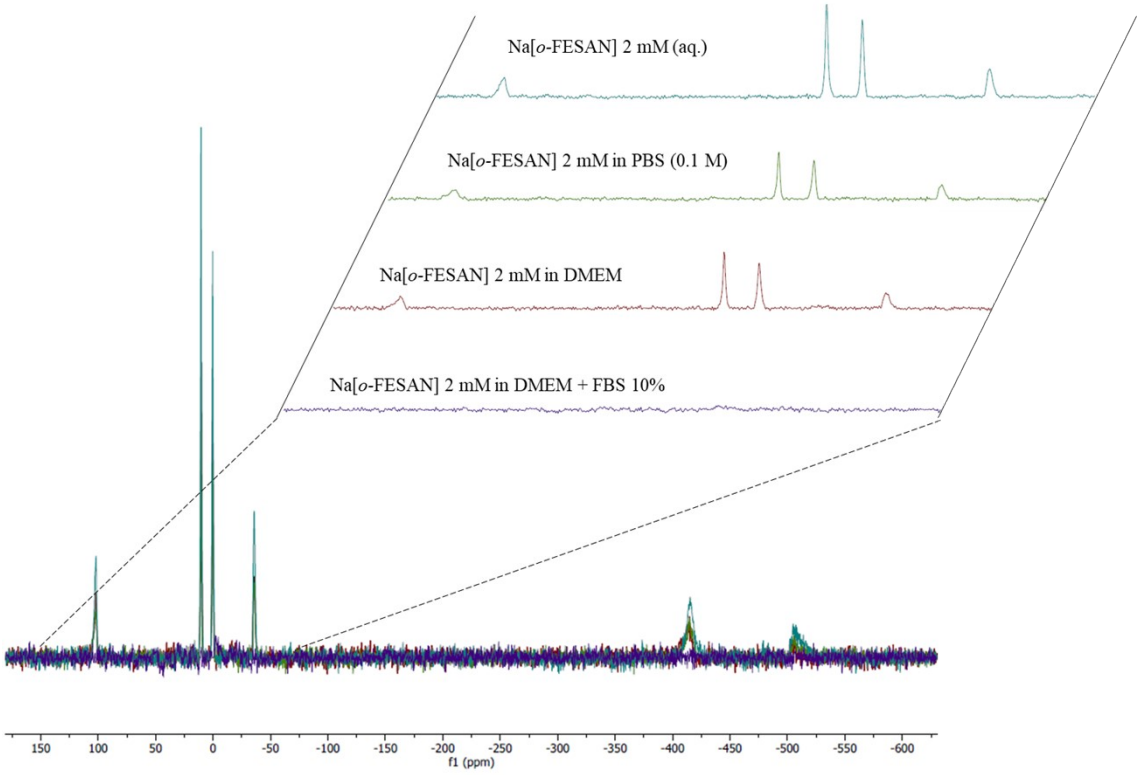
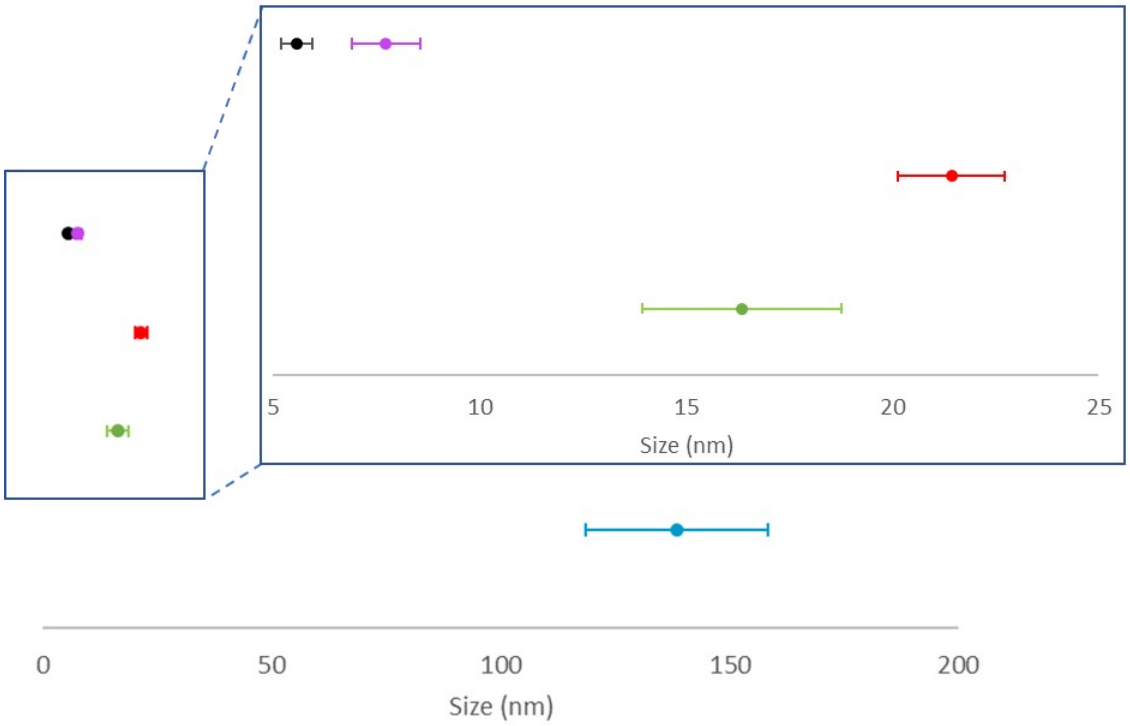


Figure S7.- DLS measurements of aqueous solution of 2 mM of Na[*o*-FESAN] in blue, in 0.1M phosphate buffer (green), in DMEM (red), in DMEM + 10% FBS (purple). DMEM + 10% FBS (black).



Na[*o*-FESAN] 2 mM (aq.): 138.4±19.9 nm (in blue)

Na[*o*-FESAN] 2 mM in PBS (0.1 M): 16.4±2.4 nm (in green)

Na[*o*-FESAN] 2 mM in DMEM: 21.4±1.3 nm (in red)

DMEM + 10% FBS: 5.58±0.38 nm (in black)

Na[*o*-FESAN] 2 mM in DMEM + 10% FBS: 7.73±0.82 nm (in violet)

DMEM and PBS (0.1 M) alone gave error measurements meaning they present no aggregates.

FBS seems to dock Na[*o*-FESAN] or either Na[*o*-FESAN] surrounds FBS since size grows 2.15 nm in presence of the metallacarborane.

References:

[i] Bennour, I.; Ramos, M.N.; Nuez, M.; Xavier, J.A.M.; Buades, A.B.; Sillanpää, R.; Teixidor, F.; Choquesillo-Lazarte, D.; Romero, I.; Martinez-Medina M.; Viñas, C. Water Soluble Organometallic Small Molecules as Promising Antibacterial Agents: Synthesis, Physical-chemistry properties and Biological Evaluation to Tackling Bacterial Infections, *Dalton Trans*., **2022**, 51, 7188–7209, DOI: 10.1039/D2DT01015A